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FINAL REPORT

REMOVAL OF ELEMENTAL MERCURY FROM A GAS STREAM FACILITATED BY A NON-THERMAL PLASMA DEVICE

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DISCLAIMER

ABSTRACT

Mercury generated from anthropogenic sources presents a difficult environmental problem. In comparison to other toxic metals, mercury has a low vaporization temperature. Mercury and mercury compounds are highly toxic, and organic forms such as methyl mercury can be bio-accumulated. Exposure pathways include inhalation and transport to surface waters. Mercury poisoning can result in both acute and chronic effects. Most commonly, chronic exposure to mercury vapor affects the central nervous system and brain, resulting in neurological damage.

The CRE technology employs a series of non-thermal, plasma-jet devices to provide a method for elemental mercury removal from a gas phase by targeting relevant chemical reactions. The technology couples the known chemistry of converting elemental mercury to ionic compounds by mercury-chlorine-oxygen reactions with the generation of highly reactive species in a non-thermal, atmospheric, plasma device. The generation of highly reactive metastable species in a non-thermal plasma device is well known. The introduction of plasma using a jet-injection device provides a means to contact highly reactive species with elemental mercury in a manner to overcome the kinetic and mass-transfer limitations encountered by previous researchers.

To demonstrate this technology, WRI has constructed a plasma test facility that includes plasma reactors capable of using up to four plasma jets, flow control instrumentation, an integrated control panel to operate the facility, a mercury generation system that employs a temperature controlled oven and permeation tube, combustible and mercury gas analyzers, and a ductless fume hood designed to capture fugitive mercury emissions.

Continental Research and Engineering (CR&E) and Western Research Institute (WRI) successfully demonstrated that non-thermal plasma containing oxygen and chlorine-oxygen reagents could completely convert elemental mercury to an ionic form. These results demonstrate potential the application of this technology for removing elemental mercury from flue gas streams generated by utility boilers. On an absolute basis, the quantity of reagent required to accomplish the oxidation was small. For example, complete oxidation of mercury was accomplished using a 1% volume fraction of oxygen in a nitrogen stream. Overall, the tests with mercury validated the most useful aspect of the CR&E technology: Providing a method for elemental mercury removal from a gas phase by employing a specific plasma reagent to either increase reaction kinetics or promote reactions that would not have occurred under normal circumstances.

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EXECUTIVE SUMMARY

Continental Research and Engineering (CR&E) and Western Research Institute (WRI) successfully demonstrated that non-thermal plasma containing oxygen and chlorine-oxygen reagents could completely convert elemental mercury to an ionic form. These results demonstrate potential the application of this technology for removing elemental mercury from flue gas streams generated by utility boilers. On an absolute basis, the quantity of reagent required to accomplish the oxidation was small. For example, complete oxidation of mercury was accomplished using a 1% volume fraction of oxygen in a nitrogen stream. Overall, the tests with mercury validated the most useful aspect of the CR&E technology: Providing a method for elemental mercury removal from a gas phase by employing a specific plasma reagent to either increase reaction kinetics or promote reactions that would not have occurred under normal circumstances.

CR&E conceptualized their technology to address the removal of elemental mercury from flue gas streams. Mercury is categorized as a high-volatile metal under Title III of the Clean Air Act Amendments of 1990 that propose the use of Maximum Available Control Technology (MACT) standards for the removal of contaminants. Mercury speciation is an important factor in appropriate removal strategies. Mercury can exist in the elemental (Hg^0) and ionic forms (Hg^{+2}, Hg_2^{+2}). Speciation is highly dependent upon the chemical environment. Mercury speciation in the atmosphere is typically quite different than from anthropogenic sources. In flue gas generated from the combustion of bituminous coals, mercury primarily exists in the ionic form, mainly as $HgCl_2$ and HgO. On average, the speciation in flue gases is 79% ionic, with the balance elemental mercury. For sub-bituminous and lignite coals, the speciation is reversed. At this point in the development of mercury removal technologies, elemental mercury is the most difficult and most costly to remove.

The CRE technology employs a series of non-thermal, plasma-jet devices to provide a method for elemental mercury removal from a gas phase by targeting relevant chemical reactions. The technology couples the known chemistry of converting elemental mercury to ionic compounds by mercury-chlorine-oxygen reactions with the generation of highly reactive species in a non-thermal, atmospheric, plasma device. The generation of highly reactive metastable species in a non-thermal plasma device is well known. The introduction of plasma using a jet-injection device provides a means to contact highly reactive species with elemental mercury in a manner to overcome the kinetic and mass-transfer limitations encountered by previous researchers.

To demonstrate this technology, WRI has constructed a plasma test facility that includes plasma reactors capable of using up to four plasma jets, flow control instrumentation, an integrated control panel to operate the facility, a mercury generation system that employs a temperature controlled oven and permeation tube, combustible and mercury gas analyzers, and a ductless fume hood designed to capture fugitive mercury emissions.

Using this facility, WRI conducted experiments that reacted a mercury-containing gas mixture with various plasma reagents to form ionic mercury compounds such as $HgCl_2$ and HgO, which can be efficiently removed from flue gas using conventional downstream technologies. The experiments used plasma reagents either diluted in a carrier gas stream or in an unadulterated form. Before working with mercury, experiments were conducted using a model compound system consisting of nitrogen and nitric oxide to gain experience in reactor operation and to evaluate the reactor's ability to efficiently mix plasma and bulk gas streams with a subsequent reaction. Additional experiments were conducted with the model compounds to establish conditions that would optimize or improve the performance of the plasma jets.

Tests with mercury used either oxygen or chlorine-oxygen compounds derived from bleach as plasma reagents. The tests using oxygen were quite successful and demonstrated the ability of a 1vol% concentration of this reagent in plasma form to completely oxidize mercury at a level of $25ug/M^3$ level in bulk gas stream. The 1vol% concentration was the lower limit of the facility's flow controllers so complete oxidation of mercury with even lower concentrations of oxygen plasma is possible. Tests with bleach-derived reagents were somewhat successful. The repeatability of the tests was poor because of a number of operational upsets that limited our ability to obtain consistent results. The reagents were obtained by bubbling nitrogen through a bleach solution. Unfortunately the sparging extracted water vapor along with the reagents. The polar nature of the water molecule acted to reduce the electrical efficiency of the jets that inhibited plasma production. WRI removed the moisture using a dry ice trap in the line feeding the jet and was able to achieve a complete oxidation of the mercury in a few experiments. However, the trap often plugged which resulted in a number of operational upsets and uncompleted tests.

Tests to improve the performance of the plasma jets succeeded in doubling the conversion of nitric oxide by nitrogen plasma compared to initial experiments. However the quantity of nitrogen needed (fed to the plasma jet) to completely convert the nitric oxide was far in excess of stiochiometric conditions. The results of our testing suggested that a different design of power supply might increase the plasma production by the jets and thereby improve conversion efficiency relative to the quantity of nitrogen fed. Presumably, the gains in efficiency would further improve the performance for mercury oxidation as well.

BACKGROUND

Mercury-Removal Technologies

Mercury generated from anthropogenic sources presents a difficult environmental problem. In comparison to other toxic metals, mercury has a low vaporization temperature. Mercury and mercury compounds are highly toxic, and organic forms such as methyl mercury can be bio-accumulated. Exposure pathways include inhalation and transport to surface waters. Mercury poisoning can result in both acute and chronic effects. Most commonly, chronic exposure to mercury vapor affects the central nervous system and brain, resulting in neurological damage.

There have been a number of attempts to regulate mercury emissions. Under Title III of the Clean Air Act Amendments of 1990, the Maximum Available Control Technology (MACT) standards are proposed. The standards identify eleven metals in the list of hazardous air pollutants (Federal Register, 1999). Six of these metals are sorted into volatility groups: high volatile (mercury), semi-volatile (lead, cadmium), and low volatile (arsenic, beryllium, and chromium). The remaining five metals are controlled as "particulate matter." MACT standards are being developed both for existing and new point sources. In principle, this will provide a technology-driven set of federal regulations. In practice, many industries will likely be unable to meet the proposed limits by using currently available technologies.

Mercury speciation is an important factor in appropriate removal strategies. Mercury can exist in the elemental (Hg^0) and ionic forms (Hg^{+2}, Hg_2^{+2}). Speciation is highly dependent upon the chemical environment. Mercury speciation in the atmosphere is typically quite different than from anthropogenic sources. In flue gas, mercury primarily exists in the ionic form, mainly as $HgCl_2$ and HgO. On average, the speciation in flue gases is 79% ionic, with the balance elemental mercury (EPA, 1997). Understanding and controlling this chemistry is critical as existing technologies are relatively effective in removing ionic mercury, but inefficient in removing elemental mercury.

Typical flue gas components can include O_2, HCl, Cl_2, SO_2, NO_2, N_2O, NO, NH_3, and H_2S. The presence and concentrations of these species can greatly enhance or complicate the mercury capture process. For example, HCl can result in the formation of $HgCl_2$ that can be effectively scrubbed or absorbed. Alternatively, other species can act as reducing agents, with the undesirable outcome of converting oxidized (ionic) mercury to elemental mercury (Galbreath and Zygarlicke, 1996).

There are a number of mercury-removal technologies available. Such technologies include adsorption, amalgamation, wet scrubbing, and electrostatic precipitation. However, the Environmental Protection Agency has recently concluded that no single technology has proven efficient for mercury capture (EPA, 1997).

Carbon filters are a common gas-treatment option. Such filters function via adsorption and are used to remove organics, heavy metals, and acid gases. In general, oxidized mercury is captured by activated carbon while elemental mercury is not. Activated carbon injection into hot flue gas has also been explored. This is limited to low-temperature operations for effective removal (<90 to 120 °C, 194 to 248 °F). Packed beds of sulfur, iodine, or chlorine-impregnated carbon have also been utilized.

Numerous other sorbents have also been tested. These are discussed in detail by Granite et al. (2000). A method for in-situ generation of sorbents has also been disclosed by Biswas and Owens (1999). In general, mercury capture by sorbents is mass-transfer limited. This is due to the low mercury concentration in high volumes of flue gas, resulting in competition with other species for active sites on the sorbent. Uncertainties also exist regarding the sufficiency of residence time in various applications. Spent carbon must also be disposed, has a finite adsorption capacity, and can potentially lead to bed fires resulting from the formation of hot spots. Disposal options include combustion, land-filling, or treatment as a hazardous waste.

Wet scrubbing is used as a gas-treatment scheme to remove acid gases, metals, particulate matter, dioxins, and furans. However, this is a very limited method for mercury capture due to the near insolubility of mercury and mercury oxide in water.

Selenium filters have been tested on flue gas streams with low Hg concentrations. However, filter lifetime is limited, the selenium filter is not re-generable, and the HgSe formed must be land-filled. Other re-generable, noble, metal sorbents, such as gold monoliths, are being developed (Durham et al., 1994), but have many of the same disadvantages.

A method for removing elemental mercury from a gas stream by an oxidation reaction to form a water-soluble mercury compound has been patented (Mendelsohn and H.-S. Huang, 1999). Aqueous iodine, bromine, chlorine, and chloric acid were described for reaction with mercury to form soluble, halogenated, mercury compounds. This invention describes the injection of the reactive solution into a gas duct using a nozzle or atomizer to generate a mist. Alternatively, the gas stream may be contacted with the reactants in a liquid scrubber. However, test results indicated that the reactions may be kinetically or mass-transfer limited, as mercury removal was suboptimal.

The chemistry of metal perchlorates has been reviewed by Gowda et al. (1984) and Pascal and Favier (1998). Gowda et al. state that a “considerable” number of mercury perchlorate complexes are known, including a number of complexes containing organic molecules. Pascal and Favier discuss synthetic methods, including the use of $HClO_4$ and Cl_2O_6 as starting materials. Fourati et al. used chlorine trioxide (Cl_2O_6) to synthesize the highly ionic compound $HgCl(ClO_4)$ (1987). Other compounds identified and synthesized include the mercury (I) perchlorate, $Hg_2(ClO_4)_2$, mercury (II) perchlorate, $Hg(ClO_4)_2$, mercury (II) oxide perchlorate, $Hg_2(ClO_4)_2 \bullet 2HgO$ (Nikitina and Rosolovskii, 1986), and hydrated mercury perchlorates.

Oxygen-chlorine reactions are particularly important in atmospheric chemistry. The experimental and theoretical literature in this area is substantial and useful in predicting and understanding the pertinent gas and liquid phase chemistry. The atmospheric chemistry of mercury and reactions with HOCl/OCl^- have been detailed by Lin and Pehkonen (1998, 1999). Ab initio methods have been utilized to investigate the gas phase properties of potentially important reactants such as O + OClO (Colussi et al., 1992) and $HClO_3$ (Francisco and Sander, 1996). The equilibrium structures $HOClO_3$ and HO_4Cl have also been examined (Francisco, 1995). This work determined that in addition to perchloric acid ($HOClO_3$), a linear chain HOOOOCl isomer (bonded dimer of HO_2 and ClO_2) is a stable structure.

Emission Reduction with Non-Thermal Plasmas

The design and function of several types of atmospheric-pressure plasma devices are well known in the general and patent literature. For example, U.S. Patent 5,414,324 describes the design of a One Atmosphere Uniform Glow Discharge Plasma device (Roth et al., 1995). The design for a non-thermal, atmospheric-pressure plasma jet has been described by Selwyn (1999). This device reports the use of activated species generated using plasma gas mixtures of CF_4/O_2/He, O_2/He, and O_2/H_2O/He. Li and Tanielian patented a hand-held, glow-discharge, atmospheric-pressure plasma device producing plasma comprised of mixtures of Ar, He, and O_2 (1999). Bittenson et al. (Bittenson, 2000) describe the generation of non-thermal plasma species introduced into a fluid medium by high-speed injection. The activated species described include monatomic nitrogen and oxygen, $OH\bullet$, $H_2O\bullet$, $SH\bullet$, $CH_3\bullet$, and other hydrocarbon species.

Non-thermal, atmospheric-pressure plasma systems have been demonstrated for emissions control by a number of different researchers. Such work has primarily targeted NO_x control (Penetrante et al., 1999). These plasmas produce highly reactive ions and metastable species to achieve chemical and thermal conversions, with gas temperatures on the order of 100 °C (212 °F). Similar devices have also been demonstrated for destruction of low concentrations of volatile organic compounds such as dichloromethane, methyl chloride, carbon tetrachloride, trichloroethane, trichloroethene, and chlorobenzene (Fitzsimmons et al., 2000). A limited amount of research has also discussed volatile metals capture. Non-thermal, plasma-based devices for mercury removal have exclusively utilized an oxygen-based, barrier-discharge-type plasma. The chemistry employed in these devices is the reaction of activated oxygen with elemental mercury to form mercury (II) oxide. This oxide particle is captured downstream using conventional means.

Alix et al. (1999, 2000) disclose an atmospheric-pressure, corona-discharge, oxygen device that can be used for mercury removal. Tests on flue gases with this system are further described by McLarnon et al. (2000). The device includes initial particulate removal in a dry electrostatic precipitator, conversion of elemental mercury to HgO via an oxygen plasma, and subsequent collection on a wet electrostatic precipitator. The reported mercury removal efficiencies range from 68–82%. The upstream filtering device is primarily used to prevent electrode fouling.

Helfritch reported a process employing the combination of a perforated corona-discharge plate and catalyst (1998). In the absence of the corona discharge, the catalyst adsorbs elemental mercury from the gas stream. When the corona-discharge device is energized, the molecules desorb and are oxidized. These mercuric oxide particles are captured using conventional, particulate-control technologies. This reactor relies upon the development and highly efficient function of a catalyst containing vanadium and titanium for the adsorption of elemental mercury. Details of the catalyst adsorption characteristics, including mercury competition with other off-gas components, are not provided.

The presence of larger particulates may prove beneficial to promote particle clustering or agglomeration. For example, such primary large particles may serve as growth sites for mercury compounds. A similar concept has been reported after plasma treatment of simulated engine exhaust gases (Hoard et al., 2000). The method of McLarnon et al. described above precludes the participation of primary flue gas particulates in a downstream agglomeration and growth scheme.

DESCRIPTION OF CONTINENTAL RESEARCH AND ENGINEERING'S (CR&E) TECHNOLOGY

A series of non-thermal, plasma-jet devices provide a method for mercury removal from the gas phase by targeting appropriate chemical reactions. This invention couples the known chemistry of mercury-chlorine-oxygen reactions with the generation of highly reactive species in a non-thermal, atmospheric-pressure, plasma device. The generation of highly reactive metastable species in a non-thermal plasma device is well known. The jet-injection device provides a means to contact highly reactive species with mercury in a manner to overcome the kinetic and mass-transfer limitations encountered by previous researchers. Active species will be selected to utilize thermodynamically favorable reactions.

Plasma gases will be generated by a combination of chemicals of the general formula $H_iCl_jO_k$. The plasma device therefore generates metastable species of the general form $H_lCl_mO_n\bullet$ that are contacted with a flue gas stream containing elemental mercury, Hg^0. The targeted reaction scheme is therefore to convert elemental mercury to a mercury oxy-chloride of the general form $Hg_xCl_yO_z$. A complicated series of reaction equations can be written. However, the elementary reaction can be generalized as:

$$Hg^0 + H_lCl_mO_n\bullet = Hg_xCl_yO_z + wH_2O \qquad (1)$$

where, the reactant subscripts are determined by the plasma gas composition. The reaction is not meant to demonstrate mass balance closure. $H_lCl_mO_n\bullet$ represents a plasma-activated species.

Figure 1 presents the free energy of formation of mercury (II) oxide and mercury chlorides as a function of temperature from 0 to 1000 °C (32 to 1832 °F). The free energy of

formation of mercury (II) oxide is greater than the free energy of formation for the mercury (I) chloride and mercury (II) chloride, so chloride formation is thermodynamically favored. In addition, this figure demonstrates that conversion of elemental mercury to an ionic form is favored at lower temperatures. This provides guidance for placement of the plasma jet device in flue gas ductwork. Since flue gas temperatures exiting a burner may be on the order of 1000 °C (1832 °F), the plasma device will likely be situated after a temperature quench step.

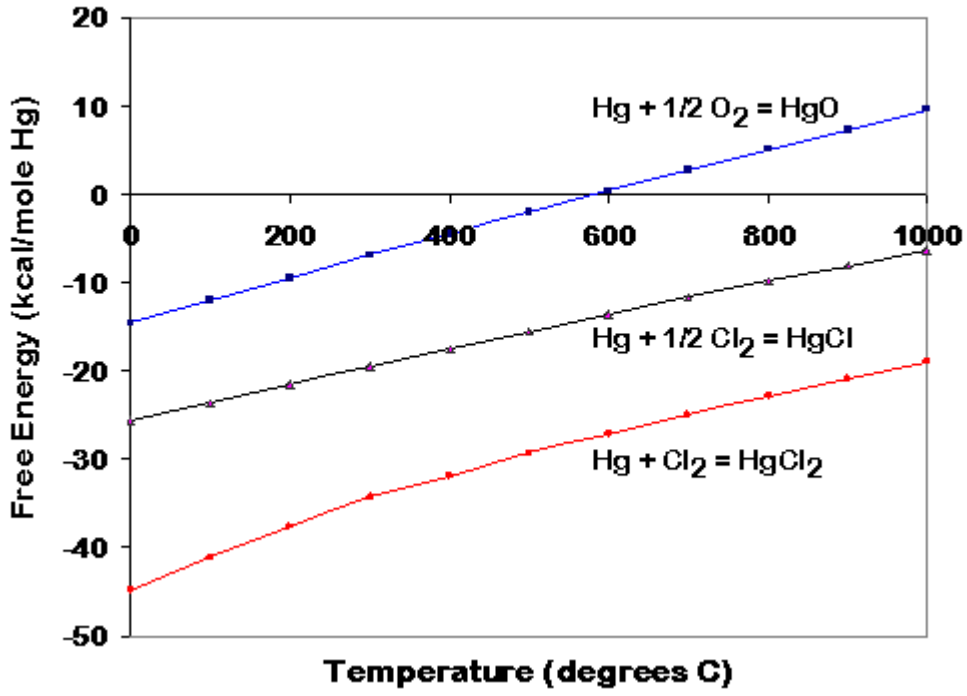

Figure 1 Plot of the Free Energy of Formation for Selected Mercury Compounds

The $Hg_xCl_yO_z$ is an ionic mercury compound that can be captured as a particle using a conventional method. Conversely, $Hg_xCl_yO_z$ may be formulated as a highly water-soluble species. In this approach, the soluble $Hg_xCl_yO_z$ can be captured in a wet scrubbing device. Figure 2 presents published water-solubility data on selected mercury compounds (Budavari ed., 1996). The target compounds for soluble species mercury removal are therefore the chloride and in particular, the perchlorate. The gas phase chemistry and targeted final removal method can be varied depending upon specific facility requirements such as existing system specifications, permitting, and other assessments.

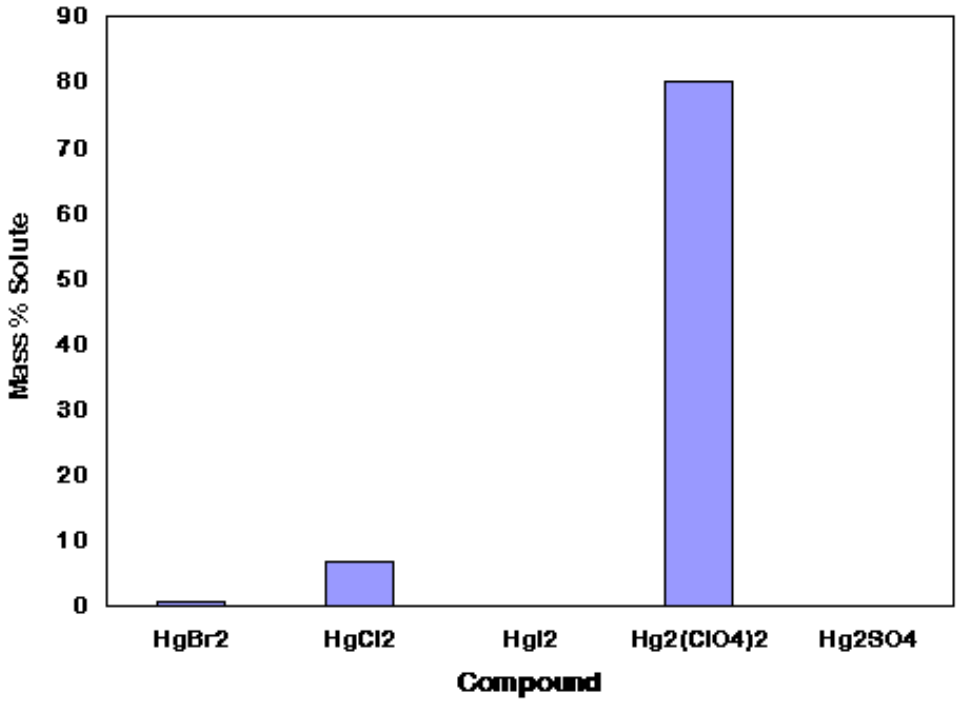

Figure 2 Plot of the Water Solubility of Mercury Bromide, Mercury Chloride, Mercury Iodide, Mercury Perchlorate, and Mercury Sulfate

This non-thermal plasma device does not rely upon a barrier-discharge design. Therefore, an upstream particulate filter may not be required and the mercury capture technique may utilize the agglomeration and growth method onto existing flue gas particles. In addition, the method does not rely upon a primary adsorptive capture mechanism; in this way, problems associated with the competition for active sites and finite adsorption lifetime are avoided. The plasma jet may be easily incorporated into existing flue gas systems and uses common gases and chemicals for reactants. In addition, it may also be used as a secondary destruction method for trace components in flue gases, such as products of incomplete combustion (PICs) and products formed from reformation and other reactions. It is possible that high destruction efficiencies may be achieved for problematic, highly toxic compounds such as polychlorinated dibenzo-para-dioxins and dibenzo furans (PCDDs/PCDFs) and polycyclic aromatic hydrocarbons (PAH).

Figure 3 presents a simple flow diagram of the technology. A flue gas containing elemental mercury flows through the duct. Inserted into the duct is a system containing a series of non-thermal, atmospheric-pressure, plasma jet devices. These devices are energized by the power supply and create activated species from chemicals delivered in vaporized or atomized form. Potential reactant chemicals may include sodium hypochlorite (NaOCl), hydrogen chloride (HCl), perchloric acid ($HClO_4$), chloric acid ($HClO_3$), chlorine trioxide (Cl_2O_6), chlorine (Cl_2), or other chemicals. These chemicals may be combined with others such as argon (Ar), nitrogen (N_2), oxygen (O_2), hydrogen peroxide (H_2O_2), water (H_2O), helium (He), or others. The

activated species react with the elemental mercury to form $Hg_xCl_yO_z$, which is captured in the removal device (i.e. electrostatic precipitator or wet scrubber). Based upon thermodynamics presented in Figure 1, extremely high process efficiencies are theoretically possible.

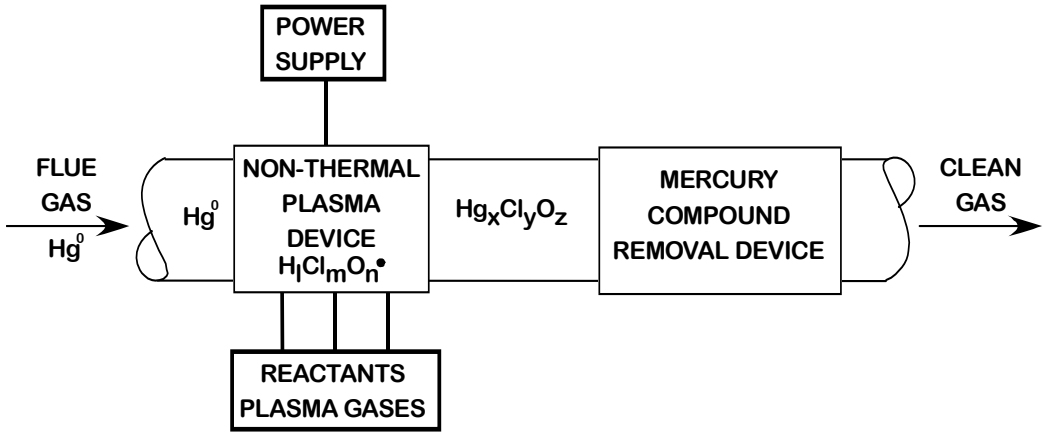

Figure 3 Simplified Flow Diagram of a Portion of a Flue Gas Treatment System, Illustrating the General Use of the Invention

DESCRIPTION OF TEST EQUIPMENT AND FACILITY

Plasma Facility and Reactor System

The conceptual design for the plasma reactor envisioned that the gas-phase reaction chemistry would be studied in a series of experiments in which plasma gas containing various concentrations of plasma reagent would contact a mercury-containing bulk gas stream. These tests would simulate a small element of cross-sectional contact between the plasma and bulk gas. The support equipment for the reactor would form the plasma facility. The functional groups of the reactor facility included mercury vapor generation, feed gas control for the plasma jets and bulk gas stream, plasma gas generation, gas-phase analytical (mercury vapor and process gas measurement), mercury collection, and the plasma reactor.

A simplified flow diagram of the plasma reactor facility as constructed is shown in Figure 4. The facility permits individual flow control (by mass flow controllers) for bulk gas and for one to four plasma gas streams. An additional flow line and controller were added to increase the concentration of (spike) the plasma reagent when necessary to completely convert the contaminant species in the bulk gas stream. The bulk gas, containing the contaminant, and the plasma streams (containing the plasma reagent) mix and react within the plasma reactor.

Two plasma reactor designs were used in the experimental work. The first-generation reactor design resembled a cylindrical pipe in shape and was custom fabricated out of Pyrex glass; its length and diameter were 24 inches and 2 inches, respectively. Ports that housed four jets were located at the mid-point of the reactor's length. The bulk gas was admitted at one end of the reactor and flowed axially along its length where it mixed with a plasma stream and subsequently exited the other end. A 2- by 3/8-inch diameter by six-inch long converging nozzle (resembling a funnel in shape) was affixed inside the reactor. The neck of the nozzle extended to a point approximately one-inch upstream of the plasma jets. The nozzle functioned to reduce the reactor's cross-sectional area and increase the velocity of the bulk gas stream just prior to its entering the plasma/bulk gas mixing region. The resulting gas mixture subsequently expanded to the reactor's original 2-inch diameter size before it exited the reactor. Four 1/8-inch diameter ports (two each on the inlet and outlet ends of the reactor, respectively) permitted sampling of the gas streams and allowed positioning of the thermocouples inside the reactor. The reactor's four plasma jet housings were located within a single plane that was normal to the axial direction of bulk gas flow. Each of the four plasma-jet housings were positioned 90 degrees from each other and thus accommodated two pairs of radially opposed jets. A picture of the first generation reactor is shown in Figure 5 (notice the nozzle to the left).

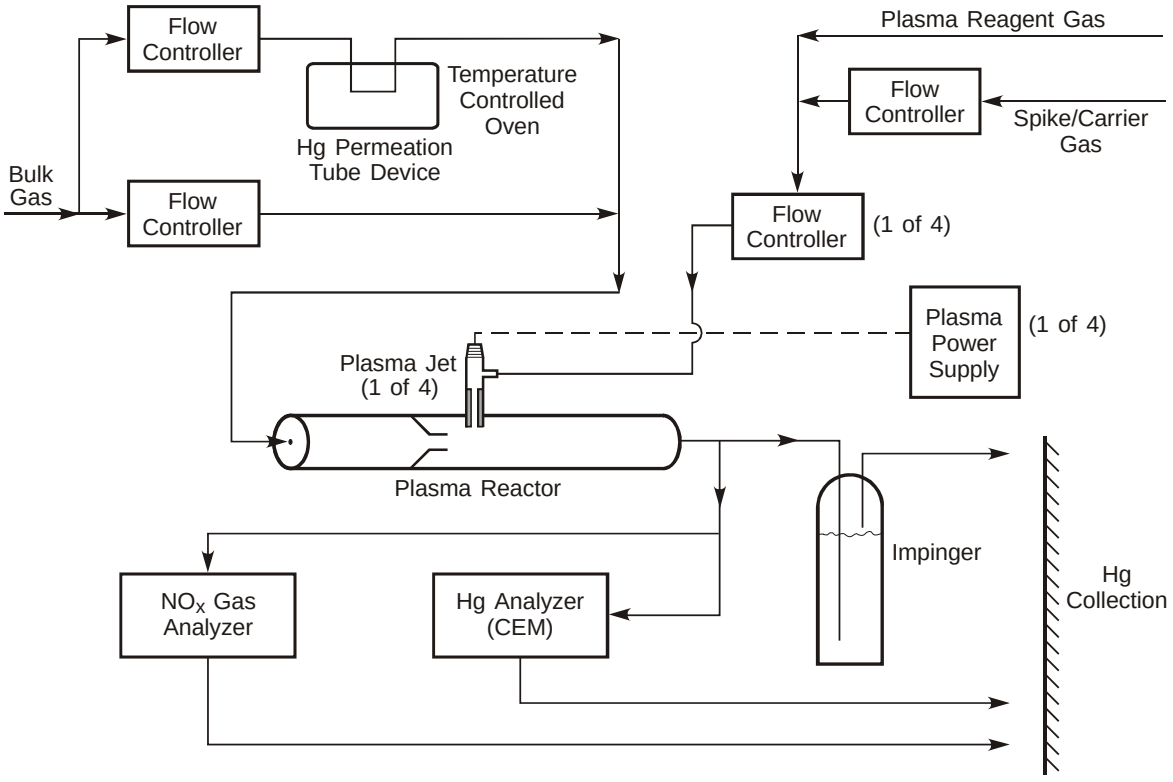

Figure 4 Block flow diagram of plasma facility constructed at WRI.

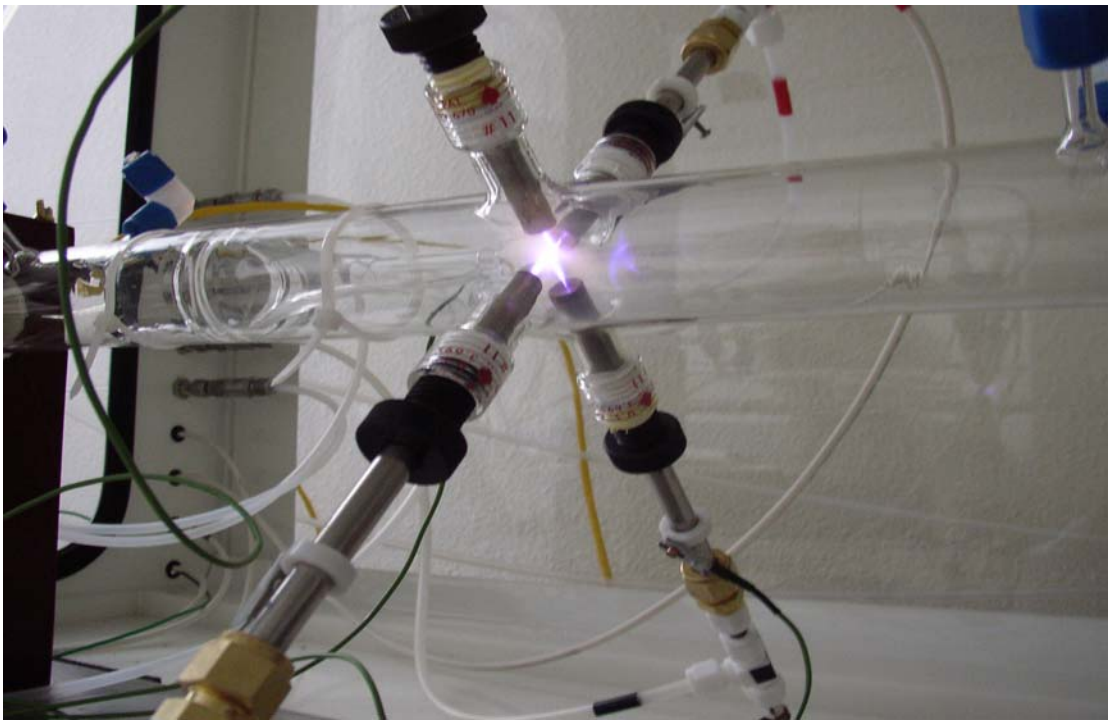

Figure 5 First generation plasma reactor in operation.

The second-generation plasma reactor was designed using CFD modeling to maximize mixing efficiency. This reactor's outward shape resembled a 2-inch diameter pipe, but employed a convergent-divergent nozzle configuration in the bulk-flow/plasma-jet mixing zone (see Figure 6). The nozzle resembled two 2- by 3/8-inch funnels joined together at their respective necks in symmetric fashion. The design accommodated four jets, each separated from its respective neighbor by 90 degrees as with the other reactor. However, the jets were angled to contact the bulk gas stream at 14 degrees relative to its axial direction of flow. This reactor was completely symmetrical in its internal construction so the plasma stream(s) could contact the bulk gas stream in either a co- or counter-current fashion, depending on the direction of flow of the bulk gas. However, the reactor was actually designed to operate in counter-current fashion. The mixing of plasma and bulk gas streams occurred just downstream (relative to bulk gas flow) of the neck of the nozzle in its diverging section. The CFD modeling indicated that the high velocity of the bulk gas stream and angle of plasma stream impingement would result in very rapid and uniform mixing.

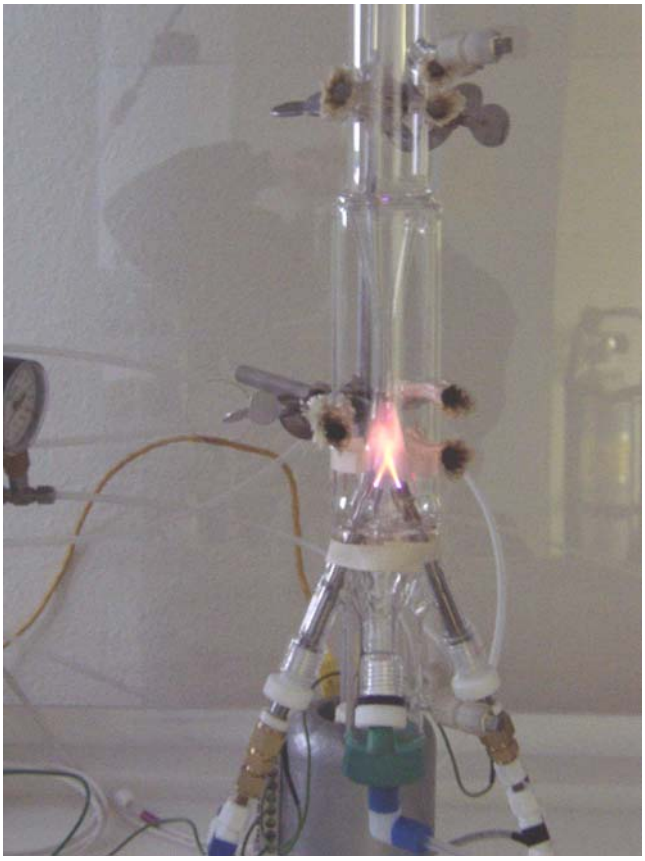

Figure 6 Second-generation reactor in operation.

The jet devices used in the reactors were constructed so that gas would flow through a continuously discharging arc before expanding through an orifice through which it subsequently exited to mix with the bulk gas. The electrical arc ionized the reagent component in the carrier gas stream to form plasma. The jets were fabricated from standard 3/8-inch O.D. by 1/4-inch I.D. 316 stainless steel tubing. The orifice plate was fashioned by welding a stainless steel cap onto one end of the tube. Machining either a 0.020-inch or 0.010-inch hole into the end cap formed the square-edged orifice. A nominal 1/4-inch O.D. by 1/8-inch I.D. ceramic liner inserted into the tubing insulated the center electrode from the outer steel sheath of the jet and provided a flow path for the gas stream containing the plasma reagent. A threaded brass union joined and sealed the open end of the steel tubing to the ceramic insulator at the point where it exited the sheath (the ceramic tube extends beyond this union fitting). Finally, a 1/4-inch plastic tee located over the exposed end of the ceramic tubing both sealed the jet from the external environment and provided coupling for electrical connection to the electrode as well as the gas delivery line. Each plasma jet was energized by a 100-watt, high-frequency-high-voltage power supply capable of generating 6-kV pulses at a frequency of 20 kHz. These unique devices were purchased from Plasma Technics Inc. Line voltage for the power supplies was controlled using a single-variable line transformer (Variac). Considerable effort has been spent in gaining experience in the construction and operation of these jets. The current version of these devices yields consistent performance both in power consumption and the quality of plasma gas emitted.

To minimize the risk of mercury exposure, all equipment that produced or contacted mercury was housed inside a ductless fume hood that employed acid-impregnated charcoal filters to remove mercury vapor. This equipment included the reactor system, mercury vapor generator, and mercury (or combustible gas) analyzer. Pass through connections for electrical cabling and gas lines were sealed with rubber gaskets. Throughout the experimental program, the fume hood worked very well and allowed sufficient space to access the reactor and its related equipment.

A control panel enclosure (located adjacent to the fume hood) integrated all the electrical devices needed to operate the reactor. These included power supply control switches and indicators including emergency shutoffs in addition to proportional control devices for the mass flow controllers, plasma power supplies, and reactor heat tapes. This panel simplified the operation of the reactor system and significantly reduced the quantity of exposed electrical wiring. A photo of the plasma facility is shown in Figure 7. This photograph shows the first-generation reactor and combustion gas analyzer in the fume hood as well as electrical control panel (to the left) and mass flow controllers (above the panel).

Figure 7 Photograph of plasma facility at WRI.

Mercury Generation and Measurement Equipment

Equipment was purchased to incorporate mercury vapor into the bulk gas stream and to measure its concentration. Specification for the quantity of mercury vapor in the bulk gas stream was based on the range of elemental mercury concentrations found in the flue gas of coal-fired utility boilers. WRI used the data set from the U.S. Environmental Protection Agency's (EPA) Technology Transfer Network Air Toxics Website. The section for Speciated Mercury

Emissions Test Reports listed emissions data from approximately 70 sites. Reviewing data pertinent to elemental mercury, WRI estimated that the emitted compositions from Powder River Basin (PRB) coals ranged from approximately 1 to 10 ppb. The range of mercury concentrations for operating the plasma reactor was extended to values between approximately 1 and 80 ppb (1 and 100 ug/M^3 based standard dry conditions).

An informal survey of literature prior to 2001 suggested that the permeation tube was the most reliable means of producing mercury vapor. Accordingly, WRI selected a Dynacalibrator device (Model 190-H from VICI Metronics) as a means of producing the needed range of vapor-phase mercury. The device holds the mercury permeation tube at a specified constant temperature, with the ability to specify the temperature from 5 to 110 degrees Centigrade above ambient. The quantity of mercury evolved from the permeation tube was a function only of temperature. Therefore WRI specified a low- and a high-evolution rate tube that when operated within the range of temperatures would allow the Dynacalibrator to generate the required levels of elemental mercury concentrations for the plasma reactor's bulk gas stream. Mercury vapor was incorporated into a gas stream as it flowed through the Dynacalibrator. In our system, a slipstream was used to pick up the mercury vapor that was subsequently mixed with the bulk gas just prior to entering the reactor.

WRI's specifications for a mercury vapor spectrometer included (1) the ability to determine mercury concentration in real-time so as to track the transient change in concentration both before and after oxidization by the plasma stream and (2) the capability of high measurement sensitivity so that the fractional reduction in elemental mercury concentration (from already low initial concentrations) could be determined as a result of plasma reactions. After considerable discussions with vendors, WRI selected a RoomSentinel from Genesis Laboratory Systems of Grand Junction, Colorado. The instrument has a sensitivity of 0.1-ug/M^3 and can sample the gas stream at rates up to once per second. In addition, the analyzer does not require calibration or zeroing between measurements or after startup. The manufacturer verifies the calibration and proper operation of the analyzer on an annual basis. This instrument worked well through out our testing and had the additional benefit of being relatively immune to the electrical interference caused by plasma generation.

RESULTS

WRI demonstrated elemental mercury could be completely oxidized using non-thermal plasma reagents formed from either oxygen or chlorine bleach. Prior to working with mercury, WRI conducted tests with a model compound system to gain experience operating the plasma jet devices, to evaluate the reactor's ability to efficiently mix plasma and bulk gas streams with a subsequent reaction, and to establish conditions that would optimize or improve the performance of the plasma jets. In fact, the majority of reactor tests conducted in this program involved tests with model compounds. This expenditure of time was not originally planned, but it reflected the fact that WRI was not able to achieve the expected conversion efficiency with the model

compounds and a significant effort was applied in attempts to resolve conversion and other hardware related performance difficulties.

Although not described in detail in this report, WRI experienced a number of operational problems with the plasma reactor system. The majority of these involved, inconsistent operation (including occasional failure) of flow control, power supply and process measure equipment. These problems were caused by the high levels of electromagnetic interference (emf/emi) generated by the high-voltage transient impulses that produced the plasma in the jets. Various methods of electrical shielding and grounding mitigated the overall severity of these problems. However in many instances, it was necessary to resolve problems on a case-by-case basis. Addressing these problems consumed considerable resources and reduced the time available to complete the planned work.

To assist WRI in the planning and conduct of tests, CR&E made available to WRI the services of Mr. Fred Becker as a consultant on this project. Mr. Becker has used non-thermal plasma jet technology to reduce pollutants from gas streams in projects for Thermal Electron and the Caterpillar Company.

Tests Using Model Compounds

Initial Tests to Demonstrate Reactor System Performance

Tests were conducted using model compounds to (1) gain experience in reactor operation (particularly the plasma jets), and (2) evaluate the reactor system's ability to efficiently mix plasma and bulk gas streams with a subsequent chemical reaction.

A model compound reaction system comprising nitric oxide (NO) and nitrogen (N_2) was used to evaluate the plasma reactor's performance. In this system nitric oxide and nitrogen reported to the bulk gas and plasma gas streams, respectively. The overall reaction for the model system is:

$$2NO + N_2^* \Rightarrow 2N_2 + O_2 \qquad (2)$$

where the (*) denotes the plasma species, nitrogen. This reaction has been frequently studied in plasma applications and thus its use provided a known basis to evaluate the conversion efficiency of the plasma reactor. The tests used nominally 400 ppm of nitric oxide in argon and 200 ppm of nitrogen in argon, which resulted in a stoichiometric mixture of reactants. Argon was used as a carrier gas because it is generally inert to plasma excitation. The high dilutions of reactant gases were used to investigate the plasma reactions at low levels of concentration, approaching that which would be employed in mercury testing.

The testing was done with one, two, or four plasma jets. The tests that employed a single jet exhibited the least and the two or four jet tests exhibited the most conversion of nitric oxide

on a basis of equivalent nitrogen injected. WRI assumed that a combination of poor mixing and a limited quantity of reagent caused the poor performance with the single jet configuration. Using that logic, it was expected that the four-jet configuration would yield the highest conversion. However, the two- and four-jet configurations converted equivalent amounts of nitric oxide. Based on these results, WRI concluded that conversion of reactant was not strongly dependent on the uniformity of contacting the bulk and plasma gas streams.

WRI had expected that under stoichiometric conditions the nitrogen plasma would substantially reduce the nitric oxide to nitrogen. In fact, initial tests converted only about 5-10% of the nitric oxide. To improve conversion, the plasma stream was spiked with increased quantities of nitrogen until all of the nitric oxide in the bulk gas stream was reacted. The nitrogen required to achieve complete conversion was a factor approximately 250 times stoichiometric. Through a trial-and-error process, the conversion of nitric oxide was significantly improved in subsequent tests by (1) adjusting the penetration of the jets into the reaction chamber, (2) refining our construction techniques for producing the jets as well as optimizing the gap between the center electrode and orifice plate, and (3) increasing the plasma power supplies from 50 to 100 watts.

These improvements resulted in complete nitric oxide conversion with nitrogen additions of 25 times stoichiometric; a ten-fold improvement compared to initial test results. The graph shown in Figure 8 shows the conversion of nitric oxide as a function of nitrogen plasma added for a test using the two-jet configuration. It should be mentioned that later in the test program the total conversion of nitric oxide required 50-to-100 times, stoichiometric additions of nitrogen for the identical experimental condition shown here. The analytical equipment and jets were rebuilt in an attempt to improve the rate of conversion, but ultimately the conversion did not improve.

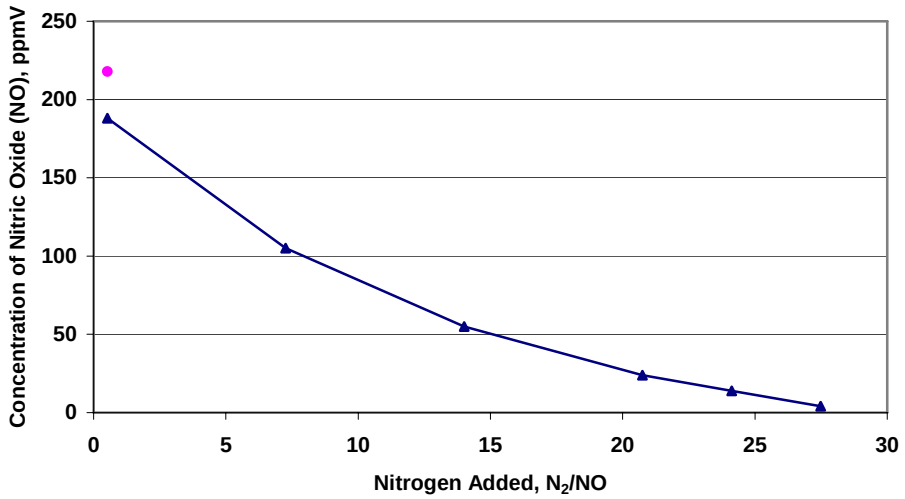

Figure 8 Conversion of Nitric Oxide Using Nitrogen Plasma

Tests were conducted by first establishing jet and bulk gas flows. The point above the curve in Figure 8 indicated that an approximate stoichiometric mixture was achieved with no noticeable reaction between nitrogen and nitric oxide. Subsequently, the jets were energized, producing plasma. The first point on the curve located at the stoichiometric mixture indicated that approximately 10% of the nitric oxide was converted by nitrogen plasma. At that point, additional amounts of nitrogen were added incrementally to the plasma stream, which increased the conversion of nitric oxide.

CR&E performed a number of numerical simulations on the reactor system. Their results suggested that the four-jet configuration would promote the greatest degree of mixing. Further, the simulations identified a region of poor mixing (a dead volume) in the reactor, which might account for the less than expected conversion of nitric oxide. This dead volume existed behind the neck of the cone, upstream of the point where the bulk gas entered the reactor and was contacted by the plasma stream. CR&E could not quantify the dead volume's effect on mixing but felt it could adversely affect the rate of dispersion of the plasma stream. WRI attempted to block off the volume using packed glass wool insulation and later a plug made of Teflon. In both cases, significantly greater amounts of nitrogen were required to completely convert the nitric oxide. These results were unexpected, but evidently the packing material acted to inhibit the plasma reaction. WRI also conducted additional tests with four plasma jets and determined that the conversion of nitric oxide was not improved significantly over to the two-jet configuration, as we had determined previously. At that point, CR&E decided to develop a second generation reactor design that used modeling calculations to optimize mixing efficiency.

The second-generation reactor used a convergent-divergent nozzle design that resembled to funnels joined at their necks. The jet's angle of impingement with the bulk gas stream was

14^{o} relative to the axial direction of bulk gas flow. The mixing of the jet and bulk gas streams occurred in the nozzle's neck region. (The section of this report that describes the reactor hardware provides a more detailed explanation of the reactor.) The reactor could be operated in either co- or counter-current configuration relative to the flow directions of the bulk and plasma streams. CR&E's modeling indicated that the most complete mixing would occur when the reactor was operated in the counter-current configuration.

The data in Table 1 compares the performance of the first- and second-generation reactors based on the quantity of nitrogen spike gas required to reduce the nitric oxide in the bulk gas stream by 98% of its original concentration. Both two and four jet configurations were evaluated. The second-generation reactor was operated in both co-current (wf) and counter-current (cc) configurations. Using the ratio of nitrogen injected to nitric oxide in the gas stream as the indicator of conversion efficiency, the data in Table 1 indicated that the second-generation reactor when operated in counter-current fashion generally performed no better than the first-generation reactor for both two and four jet configurations. With co-current flow the first- and second-generation reactors operated similarly with respect to nitric oxide conversion. The performance of the second-generation reactor was a disappointment. However, CR&E and WRI continued to believe that conversion efficiency was a function of uniform mixing and the ability of the plasma jets to generate a sufficient quantity of plasma reagent. It was decided that cold-flow testing should be conducted on the reactor to provide data for CR&E's model. These tests would involve using a visible smoke stream to determine the flow patterns developed in the reactor.

Table 1 Summary of NO conversion by N_2 plasma using two generations of plasma reactor and various jet configurations.

Reac. Type (Gen)	Flow[1] Dir.	Num of Jets	Jet Dia., in.	NO Conc., ppm	Spike N_2, slpm	Bulk Flow, slpm	Jet Flow, slpm	N_2/NO, ft_3/ft_3
1st	wf	2	0.02	387	0.050	3.50	1.75	36.94
1st	wf	4	0.02	387	0.130	7.00	1.75	48.02
1st	wf	4	0.02	331	0.090	7.00	1.75	38.87
1st	wf	4	0.02	331	0.044	3.50	0.87	38.01
1st	wf	4	0.02	331	0.084	7.00	1.75	36.28
1st	wf	4	0.02	331	0.056	3.50	0.87	48.37
2nd	cc	4	0.02	331	0.120	7.00	1.75	51.83
2nd	cc	4	0.02	331	0.080	3.50	0.87	69.10
2nd	cc	2	0.02	331	0.200	7.00	3.50	86.38
2nd	cc	2	0.02	331	0.096	3.50	1.75	82.92
2nd	cc	2	0.02	331	0.020	1.75	0.87	34.55
2nd	wf	4	0.02	331	0.074	7.00	1.75	31.96
2nd	wf	4	0.02	331	0.030	3.50	0.87	25.91
2nd	wf	2	0.02	331	0.170	7.00	3.50	73.42
2nd	wf	2	0.02	331	0.050	3.50	1.75	43.19
2nd	wf	2	0.02	331	0.020	1.75	0.87	34.55

Cold-Flow Testing

To check their mixing performance of the reactor, WRI used smoke to visually trace the path of the gas stream as it entered the reactors and was subsequently dispersed by the gas streams from the plasma jets. The intent of these tests was to identify any obvious flow mal-distribution that would result in a large portion of the bulk gas stream bypassing the mixing zone where the bulk and plasma streams co-mingled. After experimentation with several alternatives, WRI constructed a smoke generator based on heating fog juice to produce theatrical smoke. The generator was based on a design described by Shindo (1969) and involved forcing the liquid through a six-foot long, 1/16-inch I.D. stainless steel tube that was directly connected to, and controlled by a Variac transformer. This method worked satisfactorily, however producing smoke in a small, confined reactor resulted in significant water vapor condensation on the walls that occasionally obscured our vision.

Cold-flow tests were conducted on both the first- and second- generation reactors. The tests used gas rates that were similar to actual reactor operation. Bulk flow rates varied from 2 to 15 slpm and the jet rates when used were either 0.75 or 1.5 slpm. One, two, or four jets were used in the tests.

Both reactors' performances were first tested using bulk flow only. In both reactors (but to a larger degree in the first-generation design), we observed a transient condition in which the concentrated stream of smoke exited the diverging section of each respective reactor's nozzle. The stream would remain coherent until it reached approximately one or two inches from the exit of the reactor and appear to stall. Subsequently, smoke would build up from the point and back fill the volume of the reactor up to the location of the nozzle. WRI calculated the Reynolds

Number using parameters of bulk gas velocity as well as the reactor's diameter (downstream of the nozzle) and determined that the gas is flowing in a laminar-to-transitional flow regime. Therefore, it was reasonable to conclude that the transitory condition of back filling was caused by a significant reduction in velocity that results from gas expansion in the region downstream of the nozzle. In later testes, we were able to sustain a coherent stream of smoke with no back filling by employing a small vacuum pump at the discharge end of the reactor to increase the system's differential pressure. In all, no irregularities related to flow mal-distribution were noted in the flow streams developed by the bulk gas flow.

Subsequently, jet flow was incorporated into the cold-flow tests to determine if the bulk and plasma streams were mixing uniformly. WRI observed that the concentrated bulk gas stream exiting the nozzle was completely dispersed into a uniform, low-density cloud when contacted by the jet streams. These tests were qualitative, but they appeared to indicate that the bulk and jet streams were mixing satisfactorily. The possibility of inadequate gas velocity, evident in the bulk flow tests, might suggest that a reactor with a smaller cross-sectional area would be needed to achieve a higher rate. For the present, WRI planned to use a vacuum pump in the mercury testing, to increase the differential pressure (therefore velocity) across the reactor and eliminate the back filling that was initially observed. It is also possible that the pump would not be required because tests that included jet flow did not exhibit any downstream flow abnormalities. Because the cold flow tests failed to indicate flow problems, it was reasonable to suspect that insufficient power was available to convert necessary quantities of the nitrogen to plasma reagent.

Improving Performance of the Plasma Jets

A total of four test campaigns were conducted to ensure that the jets (and associated power supplies) generated a sufficient quantity of plasma. WRI investigated methods to increase plasma production by (1) optimizing energy utilization and (2) increasing the level of power supplied to the jets. The first two campaigns (described below) supported the first method of improving performance and were actually completed prior to the cold-flow testing as part of a diagnostic of system performance. The other two campaigns that supported the second method were completed just prior to commencing the mercury work.

Attempts to Optimize the Jet's Use of Power

One possible explanation for the less that expected conversion of nitric oxide was that a significant portion of electrical energy was wasted in heating the plasma reagent's inert Argon carrier gas, thus diverting energy from the production of nitrogen plasma. To investigate this possibility, WRI conducted tests that fed undiluted nitrogen to the jet. These tests used a single jet that was configured to operate at half the rate of previous tests. This was done to minimize the high nitrogen to nitric oxide ratio that would result from feeding the pure reagent. To compensate for the reduced feed rate, the jet used for these test was manufactured with an orifice diameter of 0.01-inch to maintain a high plasma discharge velocity. In spite of these measures,

the lowest achievable ratio of nitrogen to nitric oxide was 100 times greater than stoichiometic. Two bulk gas mixtures composed of either 330ppm nitric oxide in argon or 160ppm nitric oxide in nitrogen were used in the testing. The test procedure maintained a constant feed of nitrogen to the jet while varying the quantity of bulk gas fed to the reactor from approximately 3 to 20 slpm. The curves shown in Figure 9 summarize the conversion of nitric oxide achieved in these tests. The results indicated that an 80% reduction in original nitric oxide concentration required either approximately a 300- or 400-fold excess in nitrogen for bulk gases using argon or nitrogen diluents, respectively. WRI postulated that the lower conversion of nitric oxide for the bulk gas mixture using nitrogen diluent resulted from its higher disassociation energy (compared to argon). Thus, the nitrogen diluent absorbed more energy. Regardless of the curve, the results indicated that more than a thee-fold increase of pure nitrogen reagent was required to achieve a conversion equivalent to tests that used this reagent in an Argon carrier gas. The postulation of inert carrier gas adversely effecting plasma production was not supported by these tests, which was frankly surprising. However to confirm this finding, WRI needed to ensure that the jet was dissipating power sufficient to produce plasma.

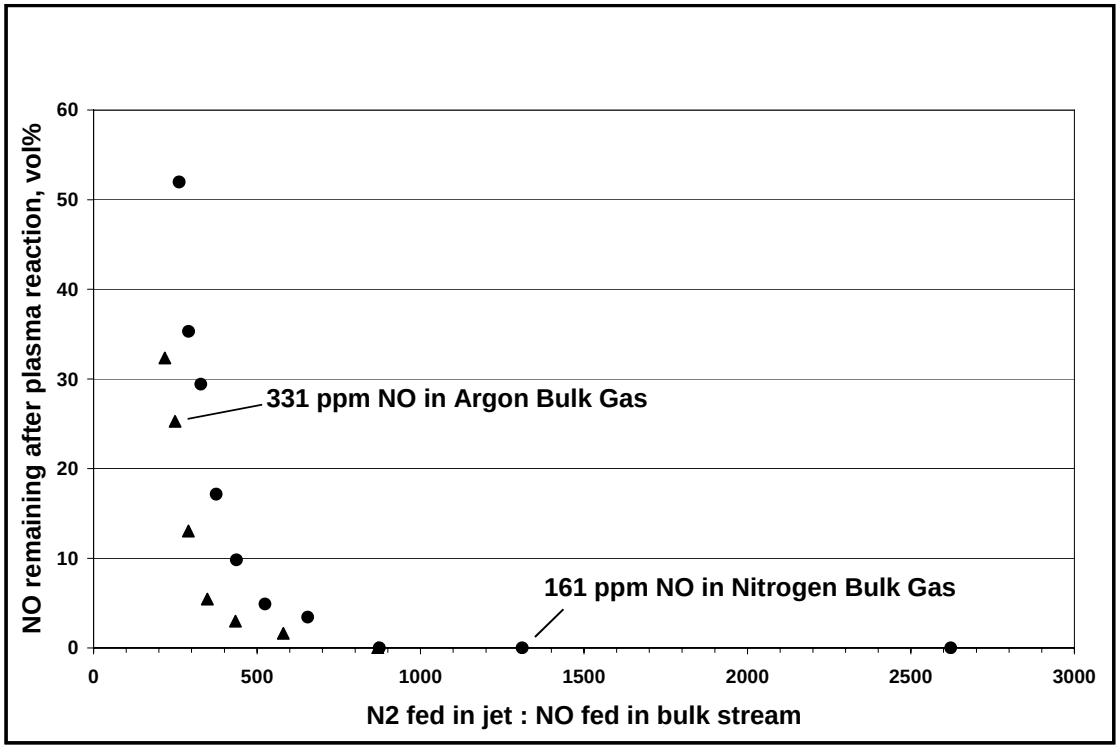

Figure 9 NO conversion using pure nitrogen in a single jet configuration.

WRI subsequently conducted tests to measure the power dissipating capacity of the plasma jet and consequently determine its ability to produce quantities of plasma necessary to convert the available nitric oxide. This was done by both measuring electrical power consumption and calculating thermodynamic energy balances of heat dissipated by the jet to the reactor system. The electrical power consumed was determined as the product of voltage and

current developed in the jet during the production of the electrical arc that forms the plasma. The thermodynamic balance calculated the power required to increase the temperature of the gas stream from reactor inlet to outlet.

For this test, WRI instrumented a single plasma jet with a dual-channel storage scope to measure the voltage traces developed between the center electrode and ground (for voltage potential) and the steel sheath to ground (for current consumption). A high wattage resistor was placed between the jet's steel sheath and the electrical ground as a means of converting current to voltage. The voltage dropped across the resistor was converted to equivalent current by the Ohm's law relationship, voltage equals current times resistance. The procedure for conducting a test was as follows: The jet was placed into the second-generation reactor that was subsequently wrapped in approximately six inches of ceramic fiber insulation, and then placed in an ice chest. Nitrogen flow rates were initiated for jet and bulk gas flow of approximately 1.2 and 3.6 slpm, respectively. The plasma jet was energized. Temperatures were measured for the inlet streams and the composite outlet stream (at the reactor's exit). After approximately sixteen hours, the reactor outlet temperature reached a stable temperature of approximately 470^{o}F and the test was terminated.

By integrating the product of voltage, times current over a complete cycle, WRI calculated the average rms power dissipation for the test of approximately 40 watts. In comparison, the thermodynamic calculation based on the temperature rise of the bulk gas yielded an equivalent power dissipation of approximately 25 watts. Ideally, both methods should result in identical values for power dissipation. The reason for the discrepancy between the two methods of calculation was not resolved conclusively. However, the consultant considered that even the lower value of 25 watts was sufficient to generate the needed quantity of plasma based on his previous work that used similar plasma jet devices.

Improve Performance by Increasing Power to the Jet

Considering all of the results to date, the most plausible alternative for converting additional nitric oxide was to increase the level of power fed to the jets. WRI had initially tuned the plasma power supplies in accordance with the operations manual, which resulted in a supply voltage of 70 volts AC, but it would be possible to increase the voltage to the supplies. In addition, the power supplies have the ability to source higher quantities of current to the jets via an adjustable control. (Again, in accordance with the manual, WRI had left this control in its centered position between minimum and maximum current delivery.) After conferring with the manufacturer, WRI decided to increase the power by first increasing the voltage, then the current.

WRI conducted a series of tests to determine the effect of increasing the supply voltage on the conversion of nitric oxide. The tests used a single 0.010-inch orifice diameter jet and the first generation reactor. The bulk and jet rates were 21 and 0.7 slpm, respectively. The bulk gas was comprised of 181 ppmV of nitric oxide in nitrogen. The results summarize in Table 2

indicated that increasing the supply voltage above 70 volts improved nitric oxide conversion; the maximum occurred at 100 volts at which point the nitric oxide concentration was reduced an additional 54% relative to its value at 70 volts.

Table 2 NO concentration as a function of power supply voltage as tested in the first generation reactor using a single plasma jet with 0.010-inch diameter orifice.

Volts Fed to Plasma Power Supply	NO Concentration, ppmV
70	115
80	94
90	73
95	68
100	62

The effects of increasing the power supply voltage on the jet's power dissipation curves are shown in Figures 10, 11 and 12. The value for power dissipated shown on each curve was determined by integrating the area under each curve. With the exception of an primary peak evident for the 70-volt curve, all of the curves exhibited generally the same shape. The spikes indicating highest power dissipation were believed to reflect the time over which the electrical arc was formed that resulted in the plasma production. Note that the width of the peak increased with increased power supply voltage.

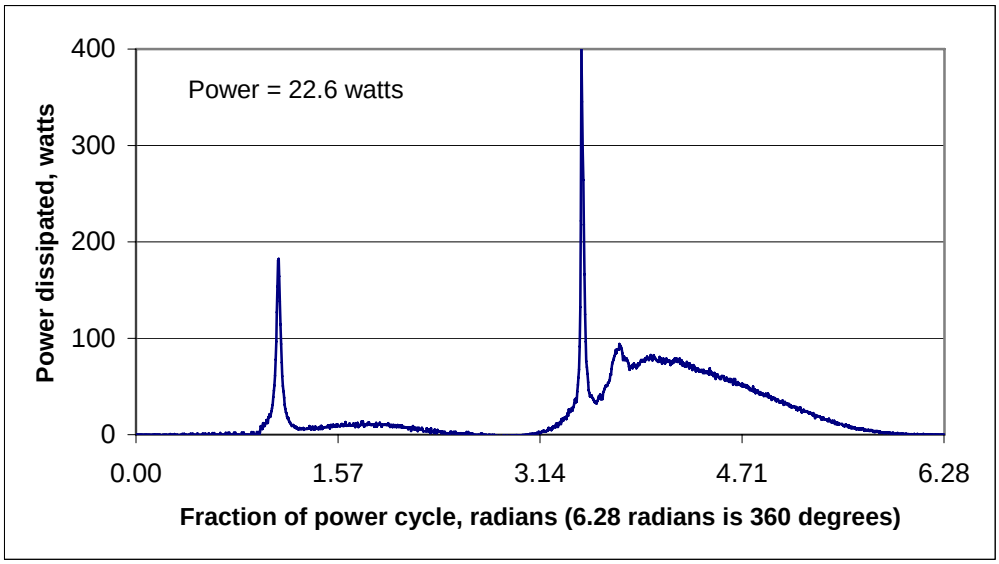

Figure 10 Power dissipation in plasma jet when power supply's fed 70 volts.

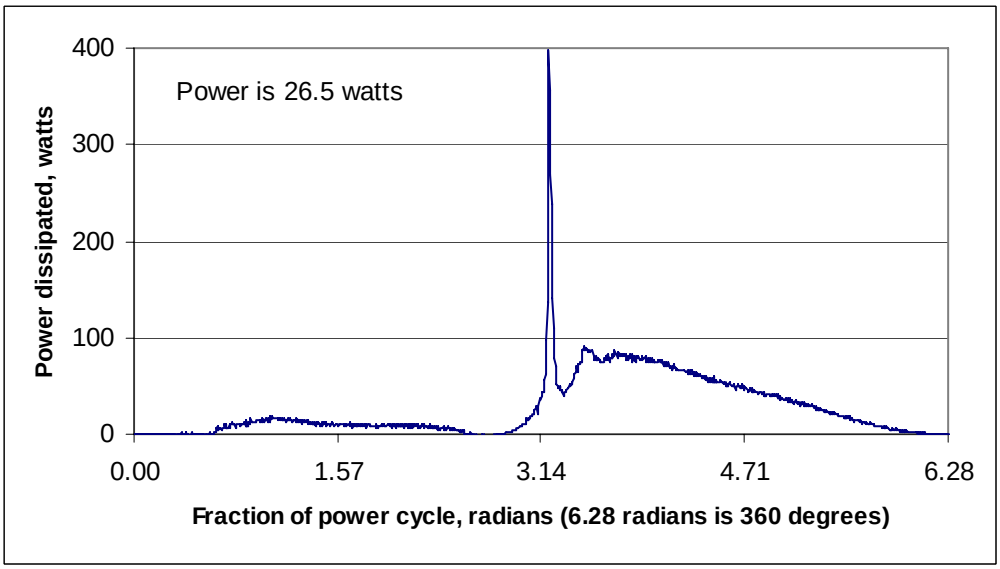

Figure 11 Power dissipation in plasma jet when power supply's fed 80 volts.

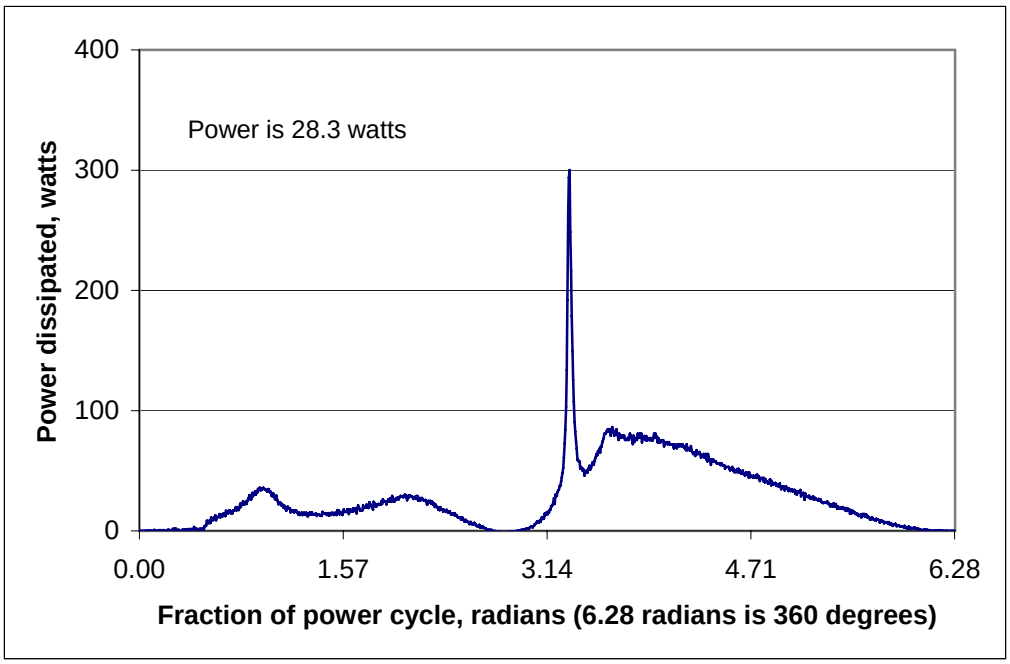

Figure 12 Power dissipation in plasma jet when power supply's fed 90 volts.

Unfortunately, operating above approximately 90 voltages significantly reduced the life expectancy of the electrodes. At 70 volts, electrodes lasted approximately two-to-four weeks. At 90 volts, the electrodes lasted for approximately two-to-three days. WRI found that nichrome wire worked best. Platinum electrodes exhibited a shorter life expectancy and inferior plasma flame relative to nichrome.

To further increase power to the jets, WRI conducted a second series of tests to increase power supply's ability to deliver additional current. The test procedure was the same as before. The power supply was sourced at 90-to-95 volts AC. Tests were conducted in which the current delivery was slowly increased. WRI continued these tests until 75 percent of maximum current capacity was achieved; thereafter testing was discontinued. Increasing current improved the nitric oxide conversion by an additional 10-to-50% percent however the operational upsets were too severe to continue.

Under conditions of increased current delivery, the electrodes were not able to survive through the completion of a test. WRI tried electrodes made of Tungsten, Molybdenum, and Platinum. In all cases the electrode tips melted (or disintegrated) and plugged the jet's orifice. This usually occurred within 10 minutes of commencing the test. As before, the best results were obtained with nichrome wire. Even with the incremental improvement in nitric oxide reduction, it was evident that the majority of the increased power was not producing plasma, but heat. WRI considered it impractical to operate under these conditions and terminated testing.

CR&E's consultant reviewed Figures 10, 11 and 12 to compare the power curves developed by the jets and at various power supply voltages. He noted that the actual on-time per cycle (duty cycle), in which plasma was produced, was quite short. Based on his experience and the shapes of the curves, he recommended that WRI use a DC-pulsed supply in which the power traces would resemble a square wave. This type of supply produced plasma for virtually the entire cycle. He also recommended that WRI try a neon or ignition transformer. He used a similar device before acquiring a pulsed supply and achieved reasonably good nitric oxide conversion. WRI investigated the possibility of acquiring a DC-pulsed supply. These devices are actually composed of a high voltage, high speed, DC supply; a pulse control device that rapidly turns the DC supply on and off; and a triggering device (such as a signal generator) that triggers (times) the pulse. The DC-pulsed supplies are obviously sophisticated, and their costs reflect this. An assembled system would cost approximately $40k with perhaps another $40k in manpower required for WRI to set up and tune properly. These expenditures would have exceeded WRI's remaining project funds.

As a practical alternative, WRI set up an ignition transformer that operated at 60 hertz, generating a peak voltage of 6kv at 25 milliamps. The experimental setup used a single jet fed with pure nitrogen at a rate of 1.5 slpm. A 0.02-inch orifice diameter jet was equipped with a nichrome electrode (our inventory of 0.01-inch jets was consumed in the previous test campaign that evaluated the effects of increased current delivery). The bulk gas contained 400ppm nitric oxide in Argon. Besides using the transformer, tests were also conducted with a high frequency

power supply operated at 90 volts AC with the current control adjusted to its mid-point position. The results of the tests demonstrated that the jet fed by the plasma power supply converted a significantly larger portion of the nitric oxide than did the ignition transformer (Table 3). The poor performance of the transformer might have resulted from its 25 milliamp current capacity; the high frequency supply could source 200 milliamp, or more. High voltage transformers are available with significantly higher current capacities (approximately 400 milliamp), but at the time that these tests were conducted, the ignition transformer's performance characteristics were considered satisfactory.

Table 3 Comparison of NO conversion using an ignition transformer or high frequency power supply.

Bulk Gas Flow, slpm	NO Concentration with Ignition Transformer, ppm	NO Concentration with High Frequency Supply, ppm
1.2	0	0
5.0	191	13
10.0	292	193

To summarize, a considerable effort was expended in attempting to improve plasma production (and therefore nitric oxide conversion) by increasing the power fed to the jets with somewhat inconclusive results. The effort succeeded in improving conversion by increasing the voltage to the high frequency power supplies. WRI further improved conversion by increasing the supply's ability to supply current to the jet, but this technique destroyed electrodes in a few minutes of operation and was not considered practical. The suitability of the high frequency power supplies for this application was not resolved. If funding and time were available WRI would have pursued the pulsed-DC power supplies (or perhaps a high voltage transformer with higher current capacity) in an attempt to increase the time over which the power supply is capable of producing plasma. Based on the power curves, the performance of plasma jets leave much for improvement.

All that can be conclusively said at this point is that WRI succeeded in slightly increasing the conversion of nitric oxide but the overall conversion, particularly considering the greater that 100:1 excess quantity of nitrogen required, remains below expectations. Our initial expectation was that the compounds would react at near stoichiometric conditions. It appeared that all of the attempts to improve the performance of the system were addressing third order effects that had little relation to improving the system's performance.

TESTS TO OXIDIZE ELEMENTAL MERCURY

Although the performance concerns with the high frequency power supplies were not resolved, WRI considered it appropriate to return to the original project plan and conduct tests with elemental mercury. CR&E and WRI decided to feed either oxygen or air or to the plasma

jets for the initial tests. If successful, the oxygen plasma reagent would oxidize elemental mercury to either HgO or Hg_2O_2. Subsequent tests would use sodium hypochlorite (NaOCl) that is found in bleach as a source of plasma reagent.

The system for generating mercury vapor was comprised of a specially designed constant temperature oven (purchased from VICI) that generated vaporous elemental mercury from a permeation tube. WRI generated the mercury-rich stream by passing approximately 0.5 slpm of either argon or nitrogen sweep gas through the oven. The resulting slipstream was mixed with the bulk gas prior to entering the plasma reactor. The reactor system used valving that permitted measurement of mercury concentration in the slipstream exiting the oven, the bulk gas stream (at the inlet of the reactor), and the product gas stream (comprised of the bulk and plasma gas streams) at the exit of the plasma reactor.

Pure oxygen was used for the initial system shakedown tests. These tests functioned well operationally, however the spectrometer indicated mercury concentrations at the exit of the reactor in the thousands of micrograms per cubic meter. These readings far exceeded its measured concentration in the inlet stream. After some investigation, WRI determined that the anomalous readings resulted from the mercury spectrometer's response to the ozone produced by the plasma jet. Literature data indicated that ultraviolet light in the range of 200-300 nm decomposes ozone to oxygen. The Genesis spectrometer employed an ultraviolet source tuned to 254 nm to induce a spectral resonance (actually an absorbance of light) in the atoms of elemental mercury to determine its concentration. Therefore, the ultraviolet source caused the ozone produced by the plasma jet to decompose to oxygen, resulting in a response in the detection band for elemental mercury. WRI eliminated the interference by decomposing the ozone in the product gas stream before it entered the analyzer. This was accomplished by heating the gas downstream of the plasma reactor to a temperature of 500^{o} F, which accelerated the rate of ozone decomposition to oxygen such that its resulting concentration no longer effected the operation of the analyzer.

With the analyzer problem resolved, WRI successfully continued shakedown tests using mercury concentrations from 50 to 200, ug/M^3 in an argon bulk gas stream. The tests used a single plasma jet fed by 1.2 slpm of pure oxygen. Equal volumes of bulk and plasma gas were fed to the reactor's mixing zone. Under these conditions the plasma reagent completely oxidized the elemental mercury (i.e. the analyzer detected no elemental mercury in the stream exiting the plasma reactor). The results from these initial tests were promising, but the proportion of plasma reagent to mercury was very high. Subsequent tests both increased the bulk gas rate and decreased the concentration of oxygen in the plasma stream.

The reactor operating conditions for test campaigns that used oxygen and sodium hypochlorite as plasma reagents were as follows. All tests were conducted in the first-generation reactor equipped with, single plasma fed at 1.2 slpm. The bulk gas rates varied from approximately 4-to-7 slpm. WRI varied the composition of elemental mercury in the bulk gas stream from approximately 5-to-50 ug/M^3 by adjusting either the rate of sweep gas to the oven or

the oven's temperature (that affected the rate of evolution from the permeation tube). Nitrogen was used as the diluent for both the bulk and jet streams. Mercury concentrations were measured using the Genesis Laboratory's Sky Sentinel CEM with its measurement sensitivity adjusted to $0.1ug/M^3$.

The tests with oxygen reagent were conducted by establishing jet and bulk gas rates then varying the oxygen-nitrogen ratio of the gas fed to the plasma jet. The blending was accomplished using the same technique employed to add spike gas in the nitric oxide tests. The mercury in the bulk gas stream for all of these tests was maintained between 15 and $25ug/M^3$. Initial tests used a 21vol% oxygen mixture (i.e. air) that completely oxidized the mercury. In subsequent tests, the volume fraction of oxygen in nitrogen was incrementally reduced to a value of 1vol%, which was the minimum rate for the oxygen stream's flow controller. All proportions of oxygen reagent when fed through the plasma jet completely oxidized the mercury in the bulk gas stream.

The operating life of the plasma jet's nichrome electrode was proportional to the oxygen concentration. At 21vol% oxygen concentrations, the plasma jet required rebuilding at approximately two-to-four hour intervals. However, the life of the electrode increased to 20 hours or longer when the oxygen concentration was less than approximately 5vol%.

Subsequently, Chlorox laundry bleach was used in tests to evaluate the effectiveness of sodium hypochlorite as plasma reagent. As it occurs in bleach, a 6wt% quantity of sodium hypochlorite (NaOCl) is buffered in an aqueous solution to maintain its high pH thus limiting its decomposition into hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), which would occur under more acidic conditions. Sodium hypochlorite solution will also degrade to evolve chlorine gas. Any of these species would be suitable as plasma reagents. However, WRI could not feed the bleach solution directly to the plasma jet because it would not operate effectively with water constituents in either liquid or vapor phase. The polar nature of the molecule would act to effectively short out the plasma jet's arc and reduce its ability to produce plasma. Instead, nitrogen gas was bubbled through the bleach solution to strip out plasma reagent constituents.

Tests using the bleach reagent were operated similarly to those that used oxygen with the exception that the stream fed to the plasma jet was first bubbled through a beaker containing approximately 100ml of bleach solution before passing to the plasma jet. We were not certain of all the specific chemical species evolved from the bleach as a result of sparging, but our noses indicated that chlorine was one of them. In an aqueous solution, NaOCl forms HOCl (hypochlorous acid), which readily degrades to form chlorine gas, oxygen and water. It is also possible that HOCl vapor existed in the stream fed to the plasma jet.

Initial tests with the bleach reagent oxidized virtually no mercury. During the conduct of the tests it was noted that the plasma flame became barely noticeable, despite the fact that the stream fed to the jet was virtually 100% nitrogen, which normally produces a bright blue flame. WRI postulated that significant quantities of water vapor were being transported from the bleach solution to the jet's feed gas stream, adversely effecting the generation of plasma. Several

methods were investigated to remove moisture from the stream. A silica gel filter inserted upstream of the plasma jet allowed the reactor to achieve an approximate 40% decrease in elemental mercury. Ultimately, WRI was able to achieve a complete oxidation of elemental mercury by using an acetone-dry-ice trap between the bleach solution and jet. WRI estimated the amount of reagent stripped from the bleach solution over a test sequence that resulted in complete mercury oxidation. By measuring the change in weights in the bleach solution and the dry ice trap, it was determined that approximately 0.02gm of material was fed to the plasma jet over an approximate four hour period of testing. This time included a number intervals over which the plasma jet was not operating to allow the system to return to an initial condition state in which no mercury was oxidized. Consequently, it would be difficult to estimate the reagent to mercury ratio. Nevertheless, the total quantity of reagent used in tests that completely oxidized the mercury should be considered quite small.

WRI was able to completely oxidize the elemental mercury in only two test sequences. The majority of tests either failed to oxidize any mercury or oxidized only 10 to 15% of the initial concentration. In addition, the tests with bleach reagent experienced a number of operational difficulties; most resulted from bypassing and plugging in the cooling traps. A possibility for improving the overall efficiency of this type of reagent producing system might be to select an alternative compound that has greater chlorine content and does not require a high degree of aqueous dilution. Alternatively, it might be possible to prepare aqueous mixtures with higher concentrations of sodium hypochlorite.

CONCLUSIONS

CR&E and WRI successfully demonstrated that non-thermal plasma containing oxygen and chloro-oxygen reagents could completely convert elemental mercury to an ionic form. On an absolute basis, the quantity of reagent required to accomplish the oxidation was small. For example, complete oxidation of mercury was accomplished using a 1% volume fraction of oxygen in a nitrogen stream. Overall, the tests with mercury validated the most useful aspect of the CR&E technology: Providing a method for elemental mercury removal from a gas phase by employing a specific plasma reagent to either enhance reaction kinetics or promote reactions that would not have occurred under existing conditions.

In addition to conducting tests with mercury, WRI attempted to establish conditions that would optimize or improve the performance of the plasma jets. This was done with a two-component model system in which nitrogen decomposed nitric oxide into nitrogen and oxygen. WRI was able to improve the conversion of nitric oxide by tuning one aspect of the plasma power supply's performance. But overall, the results of the testing were inconclusive and the complete conversion of nitric oxide required quantities of nitrogen (fed to the plasma jets) 100 times greater than stoichiometric. The initial expectation was that the model compound constituents would react at nearly stoichiometric conditions.

Based on all of the results to date and WRI's experiences in conducting a large number of tests in this program, the following recommendations are offered for advancing the technology:

- Consider employing a pulsed-DC power supply or a high-voltage, high-current transformer. The curves depicting power dissipation with the high-frequency power supply (used in this program) indicated that only a small period of the power cycle was effective in producing plasma. A supply capable of increasing the duty cycle should improve plasma production and conversion efficiency of mercury relative to the quantity of reagent fed.

- Consider redesigning the plasma reactor so that it is symmetric about a single jet. The reactor systems used in the program employed a convergent four-jet design. Results from the reactors operating at lab-scale flow rates would be difficult to scale up for commercial applications. Furthermore, many of the tests conducted in this program were ultimately operated with a single jet to achieve a more favorable reagent-to-compound ratio. Conducting single jet tests in reactors designed for four probably does not result in optimum mixing performance. Scale up would still be difficult with a single-jet system, but WRI believes that the results would better reflect the performance of a single jet in array of jets operating in a large flue duct (which would probably approximate the method of employing this technology commercially).

- Consider operating at a larger scale. WRI is concerned that the tests were operated at flow rates that were to low. With the possible exception of the nozzle/plasma mixing jet zone, the velocities developed in the reactor were in the transition region for Reynolds Number, which are not optimum for promoting efficient mixing or desirable from the standpoint of overall reactor flow performance. Consider building a system that operates with a bulk flow of approximately 50-to-200scfm in a one-to-two inch diameter pipe.

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